

## LAID-OPEN PATENT GAZETTE

*Overlaps at  
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Claim

A catalyst for hydrogenation treatment, wherein at least one kind of transition metal constituents has been fixed (carried) on fine powder of 500 m $\mu$  or less in the average particle-size by the precipitation (sedimentation) method and which is used in a suspended state in the presence of hydrogen.

Detailed description of the invention[Industrial field of application]

This invention relates to a novel fine-power catalyst suitable for being used in a suspended state in case of the treatment of hydrocarbon and the like in the presence of hydrogen.

As reactions for treating hydrocarbon in the presence of hydrogen, included (enumerated) are such hydrogenation treatment reactions of hydrogenation and the like as the hydrogenation reaction of olefin and aromatic compound(s), the demetallization reaction, desulfurization reaction and denitrification reaction, etc. of heavy oils, the hydrogenation decomposition <sup>(hydrogenolysis)</sup> reaction of such hydrocarbon and the like as heavy oils, etc., the Fischer Tropsch reaction, the methanol synthesis reaction, etc.

[Prior arts]

For effectively using an active metal(s) as a catalyst per the same weight in manufacturing a solid catalyst, it is desirable that as far as possible, the metal constituent(s) appears on the surface which is a place for reaction. For that matter, it is necessary to make the surface area of metal constituent(s) larger. Namely, it is necessary to make the particle-size of metal particles smaller. This coincides with the following: In the event that the property of solid is classified into structural sensitivity and structural insensitivity, the reactivity of solid catalysts is typical structural-sensitivity. In particular, the reaction concerned with hydrogen is said to be a reaction from which the increase of activity can be expected thanks to the surface-area increase and particle-size reduction of catalyst(s).

With regard to the relation between the surface area and the particle-size, if the particle-size is  $d(\text{m}\mu)$  and if the number (quantity) of particles is  $n$ , the average particle-size  $\bar{d}$  becomes  $\bar{d} = \Sigma nd^2$ . If the density is  $\rho(\text{g}/\text{cm}^3)$ , the surface area  $S(\text{m}^2/\text{cm}^3)$  becomes  $S = 6000/\bar{d}\rho$ .

It is therefore considered that for example, the surface area of a metal with a particle size of  $50 \text{ m}\mu$  differs by 10 times from that of a metal with a particle-size of  $5 \text{ m}\mu$  if the metal weight is the same and that a metal of  $5 \text{ m}\mu$  tends to exhibit 10-times higher activity than that of a metal of  $50 \text{ m}\mu$ .

In addition, it is said that if the particle size of a substance is made into about  $5 \text{ m}\mu$  or less by making it fine, the electron-energy level of the substance becomes discontinuous unlike bulky substances and that the properties found in case of bulky substances, e.g. the magnetic property, the optical property, etc. differ. Therefore, recently, ultra-fine particles are being expected as new functional materials, and many researches (studies) are being done. From a viewpoint of catalysts, this means that there is a possibility that if the particles are made fine, the activity of the unit surface-area, viz. the specific activity itself, and the selectivity of reaction are enhanced. Some experiments for verifying this matter are known.

Based on these matters, it is considered that making the particles of a metal constituent(s) with catalytic activity fine is an effective means for enhancing catalytic activity by decreasing the total amount of metal(s).

Recently, many trials for producing a single metal(s) itself consisting of ultra-fine particles have been being done while expecting new functional materials, and trials for applying those to catalysts have also been being done. As a typical manufacturing-method, known is a so-called in-gas evaporation method that a metal(s) is evaporated by various heating-methods and is caused to collide with the gas molecules of He, Ar, etc., to be cooled, and concentrated in a gaseous phase. And

ultra-fine metal-powder of  $20 \sim 100 \text{ m}\mu$  has been being obtained. However, the production cost is high, and in view of the industrial use of large quantities, it is considered to be too far from the practicable level. However, it is very combustible although this is a feature peculiar to ultra-fine-particle metal(s). Therefore, at a temperature of about  $200^\circ\text{C}$  or higher, it becomes impossible to expect catalytic activity due to ultra-fine particles.

To prevent the sintering among metallic fine-particles, metal particles have been being thermally stabilized in a dispersed state by keeping metal particles on a catalyst by using a catalyst, in many previous catalyst-manufacturing method. Ordinarily known is a method that to make a dispersed-metal catalyst, metal constituent(s) is carried on a mineral carrier with the large surface-area by the impregnation method or the ion-exchange method and followed by drying, baking and activation-treatment. Generally-used carriers are bulky substances, viz. so-called porous substances having the large surface-area of several  $\text{m}^2/\text{g} \sim 1000 \text{ m}^2/\text{g}$  by having the so-called porous-structure although the outer surface-area based on the particle-size is only several  $\text{cm}^2/\text{g}$ . Accordingly, also in the event that a catalytic-activity metal-constituent(s) is carried and fixed on a carrier so as to be highly dispersed and also in the event that an effect is expected by being used as a catalyst, it depends on the so-called inner surface-area just about attributable to the porous structure.

[Problems to be solved by this invention]

However, in these cases, the diffusion speed is a problem in connection with a metal constituent(s) and also in connection with a reaction substance(s). Concentration gradient arises

between each inside of porosities and the vicinity of the surface-area, thus being uneven as a place for reaction. Therefore, the effectiveness factor (effective coefficient) always becomes a problem, and as a result, such a physical structure as the size (diameter) of porosities, the distribution of porosities, the distribution of pulverized-particle size, etc. affects the dispersiveness of metal constituent(s) and the performance of catalyst(s). Furthermore, the shape and size of porosities and reactive molecules are concerned with each other, and basically, molecules larger than the porosities cannot enter into the porosities. Therefore, the property for all purposes is insufficient, and it is necessary to use a catalyst having a porosity structure suitable for respective reactions. Besides, in many hydrogenation reactions of hydrogenation and the like which are performed under heating-conditions, the vicinity of each entrance of porosities is often clogged by such a constituent with large molecular-weight as coke produced by polymerization and condensation reactions which are side-reactions. Therefore, in many cases, the catalytic action by a metal constituent(s) carried in the porosities is hindered, and so large effect as expected cannot be obtained.

For effectively using the dispersed metal carried by a carrier by solving these problems of a bulky carrier(s), it is considered that the surface area depending on the particle size (so-called outer surface-area) should be made large to highly disperse a metal constituent(s). However, in case of such a preparation method that by using fine-particle powder of 1  $\mu$  or less as a carrier, a metal constituent(s) is carried on a carrier and then, such fixing treatment as baking, etc. is done and is followed by such activation treatment as reduction, the

cohesion and autogeneous healing of fine powder are liable to arise, and it becomes difficult to keep the outer surface-area. Moreover, thereby, the metal constituent(s) tend to have autogeneous healing one another because they have not been carried (fixed) on the surface of fine powder, and the dispersibility of metal(s) becomes lower rather than that of bulky porous substances having porosities.

[Means for solving problems]

The inventors overcame these disadvantages and eagerly repeated their research (studies) about highly-active powdered-catalysts suitable for use in a suspended state. As a result, they found that aside from whether metal constituent(s) is crystalline or amorphous, in a stage where metal constituent(s) has precipitated, fine particles which have precipitated are arrested on the surface of the ultra-fine powder or in the vicinity thereof as they are, by performing, in the presence of ultra-fine powder, the precipitation (sedimentation) from a solution which is a method of precipitating very fine particles of several-hundred Å ~ several Å as unit-particles, and that because this ultra-fine powder can be used as there are, without performing fixing-treatment and activation-treatment, the cohesion and autogeneous healing of the ultra-fine powder are hard (unliable) to arise, thus enabling features as highly-dispersive-metal carrying ultra-fine powder to be fully exhibited. Thus, this invention has been completed.

Namely, this invention relates to a catalyst for hydrocarbon treatment, wherein at least one kind of transition metal constituents has been carried on fine powder of 500 mμ or less in the average particle-size by the precipitation (sedimentation) method and which is used in a suspended state in

the presence of hydrogen.

The fine-powder which plays a role as a carrier in this invention is so-called ultra-fine powder having the average particle-size (diameter) of 500  $\text{m}\mu$  or less, preferably 100  $\text{m}\mu$  or less. In proportion as the particle-size is made smaller, the effective outer surface-area which carries catalytic metal-constituent(s) becomes larger, thus being preferable.

As a process for producing fine powder, there are the break-down process for pulverizing coarse-particle powder and the build-up process for making particles by nucleus-formation and growth from molecules, ions and atoms. For effectively producing ultra-fine powder in the particle-size range of this invention, the build-up process is better.

Ultra-fine powder with the average particle-size in the applicable range is composition-wise divided largely into a mineral substance and a carbonaceous substance.

As a method of producing ultra-fine powder which is a mineral substance, there are the liquid-phase method and the vapor-phase method. In case of the liquid-phase method, ultra-fine powder can be produced by the precipitation (sedimentation) method due to co-precipitation, homogeneous precipitation, hydrolysis from alkoxide compound(s), etc. or by the solvent evaporation method due to freeze-drying, spray-drying, spray thermal-decomposition, etc.; and most of it is an oxide or a compound (composite) oxide. In case of the vapor-phase method, ultra-fine powder can be produced by the vapor-phase synthesis method due to evaporation, condensation, vapor-phase chemical-reaction or chemical vapor-deposition or by the vapor-phase cracking method due to vapor-phase oxidization, vapor-phase thermal-decomposition or vapor-phase reduction; and

oxide(s), compound oxide(s) and such non-oxide based substances as carbide, nitride, silicide, etc. are produced. In case of these ultra-fine powders, all the methods for producing fine powders which are raw materials for the materials called "new ceramics" and "fine ceramics" recently can be applied, but high purity required for these is unnecessary in this invention. As ultra-fine mineral-powder from a practical point of view, an oxide-based substance with the average particle-size of 500  $\mu$  or less consisting of silica, alumina, silica-alumina and titania which are main constituents is preferable.

On the other hand, as carbonaceous ultra-fine powder, the substances (concretely, carbon-black and thermally-decomposed carbon) formed by vapor-phase carbonization are included, out of the substances obtained by carbonizing hydrocarbon or the like. Based on the manufacturing method, carbon black is classified into oil-furnace black, gas-furnace black, channel black, thermal black, etc., and these are inexpensive ultra-fine powder being produced on an industrial scale and are available in very many kinds. Besides, the average particle-sizes of almost all kinds of carbon black are in a range of 10 ~ 500  $\mu$ , and further, in a range of 10 ~ 100  $\mu$ , and it is preferable as ultra-fine powder for use in this invention.

In addition, carbon black is preferable because surface-coarseness, viz. the ratio of the total surface-area to the outer surface area depending on particle-size, can be increased by performing oxidization-reaction. Carbon black, especially, furnace carbon-black, is positioned as a non-porous substance against generally-known bulky porous-substance. However, from a viewpoint of micro, it is fine powder having a very complicated structure consisting of amorphous portions and



finely-crystallized portions. It is considered that by being oxidized, both the amorphous portions and the finely-crystallized portions cause various oxidization-reactions, to form micro-holes not included into the concept of ordinary porosities, viz. to increase the surface coarseness in order to increase the surface area. Moreover, by the oxidization, the introduction of such functional groups as carboxyl groups, phenol-based hydroxyl groups, ether groups, etc. is brought about.

As for the oxidization method, many publicly-known methods can be applied, and oxidization is largely divided into 2, viz. oxidization in vapor-phase and oxidization in liquid phase. Namely, the vapor-phase oxidization method is a method for oxidization performed by using one kind or two kinds or more of vapor-phase oxidization agents such as molecular oxygen of air, etc., atomic oxygen, ozone, nitrogen oxide, halogen gas, etc. On the other hand, the liquid-phase oxidization method is available in the following:

- \* Method of performing oxidization by using one kind or 2 kinds or more of such chemicals as nitric acid, potassium permanganate, chloric acid, soda hypochlorite, etc.
- \* Method for performing electrolytic oxidization by using various electrolytes such as acid, alkali, salts, etc.

Regarding the extent of oxidization-reaction, from a practical point of view, adequate conditions should be selected in view of the balance among the decrease in mass and the increase in the surface area and the extent of functional-group introduction. Anyway, carbon black and all brought about by oxidizing carbon black can be included as the fine powder of this invention.

The metal compounds used as raw materials for being carried on these fine powder are selected from compounds containing at least one kind or more of transition metals in the periodic table of elements. Concretely, transition metals are

Cu, Ag.

Au, Zn, Cd, Hg, Sc, Y, La, Ac, Ti, Sr, Hf.

V, Nb, Ta, Cr, Mo, W, Mn, Fe, Co, Ni.

Ru, Rh, Pd, Os, Ir, Pt

And especially out of these, it is preferable to use one or more compounds containing one kind or more of metals selected from Cu, V, Cr, Mo, W, Fe, Co, Ni, Rh, Pd and Pt. With regard to compound compositions, ones selected from organic metal compounds, metal complex compounds, inorganic metal salts, etc. are acceptable, and concretely, available are compounds containing alkyl groups, allyl groups, cyclopentadienyl groups, etc. as ligands, carbonyl compound, hydroxide, alkoxy compound, diketone compound such as acetylacetonate complex, organic carboxylic-acid compound, organic sulfonic acid or organic sulfinic-acid compound, amine compound such as organic diamine complex, phthalocyanine compound, nitrile or isonitrile compound, amine compound such as dithiocarbamate complex, phosphine compound, heteropolyacid compound, carbonate, carboxylic-acid salt, sulfate, nitrate, hydroxide, halogenite, etc. The forms of these transition-metal compounds should not be stipulated, but for use, it is indispensable to dissolve them into a solvent-to-be-used, in the following catalyst-preparation method.

In the event that the present-invention catalyst with high activity is produced, it is necessary to carry out the so-called precipitation (sedimentation) method for precipitating a

constituent(s) containing a transition metal(s) onto fine powder. Such a method as to carry transition-metal compound(s) on fine powder by any of various impregnation methods or the ion-exchange method which are generally-known solid-catalyst preparation methods, and then perform the baking and activation-treatment is not preferable. Recently, as a method of carrying a metal(s) with it highly-dispersed, on a bulky porous mineral-carrier, a method and so on for baking after being impregnated in an organic solvent, using a metal carbonyl-cluster compound(s) or an organic metal compound(s), etc., have been being contrived, but are not preferable as the present-invention method where the ultra-fine powder is used as a carrier.

The reason why these ordinary solid-catalyst preparation methods are not preferable is considered to be that each particle of the fine powder which plays a role as a carrier is very fine (small). Namely, in the catalyst-preparing method based on various impregnation methods or the ion-exchange method, the promotion is considered to be done especially in the concentration process and the drying process. However, the fine powder is not considered to exhibit sufficient carrier-action for carrying with high dispersion while preventing the cohesion of metal compounds, and in addition, the metal compound(s) are considered to tend to cause the cohesion and adhesion of the fine powder by conducting binder-like action together with the medium against the fine powder. Moreover, in the baking process being generally carried out as the treatment for fixing a metal compound(s) on a carrier, the adhesion and sintering of the fine powder are caused, and this phenomenon is considered to be further promoted by the catalytic action of the carried metal(s).

These matters are not desirable, because the highly-dispersive carrying of metal constituent(s) on the surface of the fine powder and in the vicinity thereof tends to be hindered by the features of the large outer surface-area based on the fine particles of the fine powder.

On the contrary, in case of the catalyst-manufacturing method of this invention, the transition metal compound(s) can be maximally carried by the features of the fine powder. Namely, the production method of the present invention is a precipitation (sedimentation) carrying method for precipitating a transition-metal constituent(s) by adding a precipitation agent after dispersively mixing the fine powder by fully soaking it into a solution with one kind or more of transition-metal compounds dissolved.

Solvents for dissolving transition-metal compounds can be classified into aqueous solvents and organic solvents. However, for alleviating the cohesion of fine powder, organic solvents are comparatively preferable. Concretely, usable are such alcohols and the like as methanol, ethanol, propanol, phenol, cresol, ethyleneglycol, propyleneglycol, etc., such ether and the like as diethyl-ether, dioxane, tetrahydrofuran, etc., such ketone and the like as acetone, methylethylketone, pentanone, etc., such halogenated carbons and the like as dichloromethane, chloroform, carbon tetrachloride, dichloroethane, etc., such hydrocarbon and the like as hexane, heptane, benzene, toluene, xylene, etc., such fatty acid and the like as acetic acid, propionic acid, etc., such ester and the like as methyl acetate, ethyl acetate, etc., such nitrogen-compound based solvents as acetonitrile, triethylamine, butylamine, pyridine, etc., such sulfur-compound based solvents as carbon disulfide, thiophene,

dimethyl sulfoxide, etc.

With regard to these organic solvents, those high in dissolvability for a transition-metal compound(s)-to-be-used or a precipitation agent(s) as the case may be, are selected, and to prevent the solvent(s) from remaining on (in) the catalyst, those high in stream pressure and low in the boiling point are preferable.

In the event that the fine powder is suspended in a solvent, it can be suspended in a solution with one kind or more of transition-metal compound(s) dissolved, or after suspending the fine powder in a solvent itself, a solution with one kind or more of transition-metal compound(s) dissolved can be added. In short, it is necessary to fully soak, disperse and mix the fine powder. For this, a publicly-known dispersant and so on can be used.

With reference to the precipitation method of precipitating a transition-metal constituent(s) by adding a precipitation (sedimentation) agent to a suspension solution in which the fine powder has been dispersively mixed, any of all methods known as the precipitation (sedimentation) method can be applied. Concretely, the following can be applied.

- \* Homogeneous precipitation method for producing a precipitation agent by chemical reaction in a solution in order to eliminate the local unevenness of the precipitation agent
- \* Method of hydrolyzing organic metal-compound(s) such as metal alkoxide and metal acetylacetae, etc. and metal complexes
- \* Co-precipitation method for precipitating the even (uniform) mixture of each constituent from a solution containing 2 kinds or more of metal compounds.

- \* Method of precipitating the metal constituents of a reduced state and sulfide by conducting reduction-reaction using various reduction agents, hydrogen-gas, hydrogen-sulfide gas, etc.
- \* Method for precipitating metal constituent(s) by the decomposition-precipitation reaction of metal compound(s)
- \* General precipitation (sedimentation) method of precipitating metal constituent(s) by the mutual direct-reaction of metal ions and precipitation-agent ions.

Namely, it is considered that by conducting the precipitation (sedimentation) reaction in a fine-powder suspended liquid of a dispersed state, the fine powder inhibits the cohesion and autogeneous healing of the produced fine-particle nucleuses of metal constituent(s), which will arise during the precipitation-reaction and in the treatment-process-after-that, and that the fine powder exhibits its function of protecting in a state of fine metal-constituent(s). The compound compositions of the metal constituent(s) which precipitated are such single kinds as hydroxide, oxide, sub-oxide (low-grade oxide), sulfide, boride, phosphide, reduced metals, etc., and mixed kinds and composite kinds.

After the precipitation-reaction is over, the solid and the liquid are separated by the conventional publicly-known filtration and centrifugal separation, and by washing and drying, the fine powder which has carried one kind or more of transition-metal constituents is obtained. This obtained fine-powder can be used as a suspended catalyst as it is. In particular, the fine powder obtained by precipitating sulfide and a compound(s) mainly containing a metal constituent(s) of a reduced state has especial-high activity as a catalyst to be

used for treating hydrocarbon in the presence of hydrogen. In case of the present-invention catalyst, the baking for fixing a metal constituent(s) to a carrier as done in the ordinary catalyst-manufacturing method should not be done. However, hydrogen reduction and the sulfurization treatment, etc. for catalyst activation can be done in a range (domain) of comparatively-low temperature.

It is preferable that the amount of the metal constituent(s) precipitated onto the fine powder, viz. the carried amount thereof is 0.1 ~ 50 wt% based on the weight of the fine powder in terms of metal(s). If less than 0.1 wt%, the catalytic activity of the metal cannot be fully obtained, and if more than 50 wt%, the catalytic activity of the metal(s) is not enhanced so much compared with the amount of the metal(s) used. Rather, in the stage of catalyst-production, the cohesion and autogeneous healing of the fine powder arise, and consequently, the feature of use of the fine powder becomes dim.

The concrete kind and combination of metals, the chemical composition of the carried metal-constituents, the kind of the fine powder, the kind of the fine powder, the amount of the metal(s) carried on the fine powder, the amount used as a catalyst, etc. can be optionally selected based on the purpose of use of the catalyst, the kind of the raw material treated, the conditions of use, etc.

[Effect of the invention]

As can be seen from the examples and the comparative examples, the present-invention catalyst with dispersed metal-constituent(s) is excellent in the catalytic effect of the reaction for treating hydrocarbon and the like in the presence of hydrogen.

### [Examples]

This invention is described in more detail based on the examples, but this invention is not limited by these examples.

#### Examples 1 ~ 11

The metal compounds (raw materials), precipitation-agents and solvents used in the respective examples, and the metal constituents carried by the fine powder precipitated by the precipitation (sedimentation) reaction, and the carried amounts, are shown in Table 1. In addition, the kinds of the fine powders used in the respective examples, the average particle-sizes (diameters) thereof measured by an electronic microscope (E.M.), and the surface-areas measured by the BET method, are shown in Table 2.

Each catalyst-manufacturing was carried out by the following method.

The metal compound was completely dissolved in a large amount of solvent, and into this diluted solution, carbonaceous fine-powder or fine mineral-powder were fully dispersed. This suspended solution was fully stirred and mixed, and in this state, the metal constituent(s) with the predetermined composition was precipitated by gradually dripping a solution consisting of a solvent having a liquid or solid precipitation-agent dissolved, and in case of a gaseous precipitation-agent, it was blown into the suspended solution. In this case, it is necessary to add a sufficient amount of precipitation-agent for fully precipitating the metal constituent(s) having the predetermined composition. Besides, the precipitation (sedimentation) was done at a temperature between 10°C and 100 °C. After completion of the precipitation-reaction, the filtration was done, and the solid was fully washed with



the solvent used, and further, it was fully washed with methanol. Thereafter, the solid was dried at a temperature between 100 °C and 150°C under reduced pressure, to obtain a fine-powder catalyst carrying a dispersed metal-constituent(s). The fine powder which is the raw material, and the manufactured catalyst, were examined through a microscope in order to compare the average particle-sizes, and as a result, no meaningful difference was observed.

Table 1

<u>Examples</u>	<u>Atmosphere</u>	<u>Solvents</u>	<u>Metal compounds</u> <u>as materials</u>
1	Air	Ethanol	
2	Air	Acetone	$\text{CrSO}_4 \cdot 5\text{H}_2\text{O}$
3	Air	Water	$\text{VO}(\text{C}_2\text{H}_3\text{O}_2)_2$
4	Air	Methanol	$\text{MnO}_2 \cdot 2\text{H}_2\text{O}$
5	$\text{N}_2$	Ethanol	$\text{Fe}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$
6	Air	Methanol	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$
7	$\text{N}_2$	Ethanol	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ $\text{Mo}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ $\text{Mo}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ $\text{Mo}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$
8	$\text{N}_2$	Ethanol/water (Ratio by weight: 1/1)	$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$
9	$\text{N}_2$	Ethanol/water (Ratio by weight: 1/1)	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$
10	$\text{N}_2$	Ethanol/water (Ratio by weight: 1/1)	$\text{H}_2\text{P}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$
11	Air	Methanol	$\text{LiClO}_4 \cdot 7\text{H}_2\text{O}$

Table 1

<u>Examples</u>	<u>Precipitation agents</u>	<u>Metal-constituents carried and amounts carried (wt% in terms of metals)</u>
1		Copper sulfide*
2	(NH <sub>4</sub> ) <sub>2</sub> S	Vanadium sulfide* (15)
3	H <sub>2</sub> S	Molybdenum sulfide* (6)
4	W <sub>2</sub> S <sub>3</sub>	Iron sulfide* (2)
5	Na <sub>2</sub> SO <sub>4</sub>	Cobalt boride (15)
6	H <sub>2</sub> S	Nickel sulfide - Molybdenum sulfide* (2)
7	Na <sub>2</sub> SO <sub>4</sub>	Nickel boride* (3)
8	H <sub>2</sub> SO <sub>4</sub>	Rhodium (4)
9	H <sub>2</sub> SO <sub>4</sub>	Palladium (7)
10	H <sub>2</sub> SO <sub>4</sub>	Platinum (6)
11	(NH <sub>4</sub> ) <sub>2</sub> S	Lanthanum sulfide* (12)

\* The composition is not constant, and S or B / metal-atom ratio has a range (scope).

Table 2

Specific surface-area  
Average particle-size  
Kinds of ultra-fine powder  
Examples

例	超微粉の種類	平均粒径(μm)	比表面積(m <sup>2</sup> /g)
1	カーボンブラック	1.5	250
2	カーボンブラック	1.6	210
3	カーボンブラック	2.0	150
4	カーボンブラック	3.0	90
5	カーボンブラック	4.0	60
6	カーボンブラック	4.0	160
7	カーボンブラック	6.5	120
8	SiO <sub>2</sub>	7	550
9	SiO <sub>2</sub>	12	250
10	SiO <sub>2</sub>	16	150
11	Al <sub>2</sub> O <sub>3</sub>	20	90

Carbon black.

■ 気相酸化処理したもの  
Oxidized in vapor phase

## Examples 12 ~ 18

To examine the catalytic effect for the treatment of hydrocarbon and the like in the presence of hydrogen in connection with the dispersed-metal-constituent carrying fine-powders manufactured in Examples 1 ~ 7, hydrogenolysis reaction was carried out using a heavy residual-oil as a raw-material oil. The property of the heavy residual-oil is shown in Table 3. As for the experiment method, a stirring-type autoclave with an inner volume of 500 ml was charged with a raw-material oil and 2 wt% (against the raw-material oil) of the catalyst, and the hydrogen pressure of 150 kg/cm<sup>2</sup> was blown in and was sealed. While being stirred at a revolution speed of 1000 rpm, the reaction was done for 1 hour at 450°C.

One hour of the reaction time was regarded as the experiment time, and the compensation for the time needed for rise and cooling was not taken into account. The produced oil after the reaction was recovered in all, for analysis. The results of Examples 12 ~ 18 are shown in Table 4 together.

Table 3

Boiling-point range:	440°C +
Specific gravity (15/4°C)	1.054
H/C	1.40
Sulfur (wt%)	4.66
Nitrogen (wt%)	0.76
V (ppm)	726
Ni (ppm)	145
Asphaltene Ca + ) (wt%)	22.3

Comparative Examples 1 - 4

These were carried out by the same experiment method as that of Examples 12 ~ 18. In case of Comparative Example 1, no catalyst was used. In case of Comparative Example 2, the experiment was carried out by adding 2 wt% of a porous  $\gamma$ -alumina catalyst (pulverized so as to become about 10 ~ 60  $\mu$ ) with the specific-area of 220 m<sup>2</sup>/g (BET-method) containing 4 wt% of nickel oxide and 15 wt% of tungsten oxide. In case of Comparative Example 3, the experiment was performed by adding 2 wt% of a ball-mill pulverized CuO/SiO<sub>2</sub> (Cu-content: 12 wt%) catalyst obtained by impregnating a copper acetylacetonato (phonetically-spelled) complex with fine-powder silica [average particle-size: 16 m $\mu$  (E.M. method); specific

surface-area:  $150 \text{ m}^2/\text{g}$  (BET-method) ] in ethanol by the solvent evaporation method, and then, drying it and baking it at  $500^\circ\text{C}$ . In case of Comparative Example 4, the experiment was conducted by adding 2 wt% of a ball-mill pulverized  $\text{MoS}_2/\text{Al}_2\text{O}_3$  (Mo-content: 4 wt%) catalyst obtained by impregnating hexacarbonyl-molybdenum with fine-powder alumina [average particle-size:  $20 \text{ m}\mu$  (E.M. method); specific surface-area:  $90 \text{ m}^2/\text{g}$ ] in toluene by the semi-drying carrying method, and then drying it and baking it at  $500^\circ\text{C}$  and then treating it by hydrogen sulfide at  $500^\circ\text{C}$ . The respective experiment-results are shown in Table 5.

As is obvious from the results of Examples 12 ~ 18 and Comparative Examples 1 ~ 4, it can be seen that the dispersed-metal-constituent carrying catalyst of this invention is excellent in the catalytic effect for the reaction for treating hydrocarbon and so on in the presence of hydrogen.

Table 4

Examples		12	13	14	15	16	17	18
Catalysts	Ex. 例	CuSx/C	VSx/C	MoSx/C	Asx/C	CuSx/C	NiSx-MoSx/C	NiSx/C
Cracking (decomposition) rate (wt%)	Ex. 例	(4)	(5)	(6)	(4)	(5)	(4)	(7)
Desulfurization rate (wt%)	440°C, 分解率 (重量%)	71	74	73	68	76	75	74
Metal removal (Ni+V) rate (wt%)	脱炭素 (重量%)	61	63	68	59	66	71	78
Asphaltene removal rate (wt%)	脱炭素 (重量%)	92	87	96	86	97	94	93
Amount of coke generated (wt%)	1) 脱炭素 (重量%)	73	74	78	64	74	76	78
Sticking of solid on the wall	2) コークス発生量 (重量%)	8.4	4.2	2.4	4.2	2.2	2.1	2.8
	3) 脱炭素 (重量%)	Nil	Nil	Nil	Nil	Nil	Nil	Nil

1) アスファルテンはヘキサン不溶、テトラヒドロフラン溶解として定数。  
 2) コークスはテトラヒドロフラン不溶分のうち仕込み触媒量を差し引いたものとして定数。  
 3) 固形物の壁面付着がある場合は、連続装置による反応においては、反応後の固形物が回収可能な場合が多い。

- 1) It is defined that asphaltene is not dissolved in hexane but is dissolved in tetrahydrofuran.
- 2) It is defined that coke is the residue after deducting the amount of the charged catalyst from undissolved tetrahydrofuran.
- 3) In the event that solid has stuck on the wall, the possibility that the reactor is closed is high, in the reactor by a continuous apparatus.

Table 5

Comparative examples

表 5

比較例	1	2	3	4
Catalysts → 触媒	Ni	NiO-WO <sub>3</sub> -Al <sub>2</sub> O <sub>3</sub>	CoO/SiO <sub>2</sub>	MoS <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>
Cracking (decomposition) rate (wt%) → 440℃分解率 (wt%)	6.8	7.8	6.7	7.5
Desulfurization rate (wt%) → 脱硫率 (wt%)	8.8	6.8	6.6	5.2
Metal removal (Ni+V) rate (wt%) → 金属 (Ni+V) 除去率 (wt%)	5.8	8.8	6.8	5.4
Asphaltene removal rate (wt%) → アスファルト除去率 (wt%)	2.1	3.4	4.8	3.1
Amount of coke generated (wt%) → コーク生成量 (wt%)	18.2	2.5	12.8	7.4
Sticking of solid on the wall → 固体の壁付着の有無	Occurred 有	Occurred 有	Occurred 有	Occurred 有